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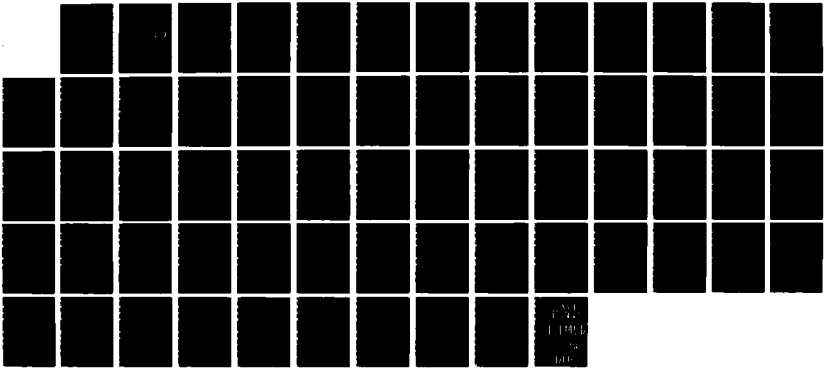

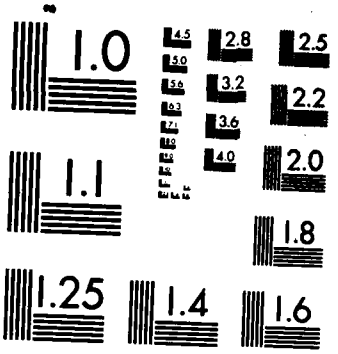

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REPORT No. ONR-2-8 (Interim)

PERIOD COVERED: 1 January 1985 through 31 December 1985

RESEARCH IN ENERGETIC COMPOUNDS

A Report on Work Sponsored by the
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Contract N00014-78-C-0147
NR 659-796/10-26-84 (430)

February 1986

FLUOROCHEM, INC.

680 South Ayon Avenue
Azusa, California 91702

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by

T. G. Archibald, L. C. Garver, M. P. Cohen, and K. Baum

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: ONR-2-8	2. GOVT ACCESSION NO. AD-A164 301	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Research in Energetic Compounds		5. TYPE OF REPORT & PERIOD COVERED: Interim Summary 1 Jan 1985 - 31 Dec 1985 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): T. G. Archibald, L. C. Garver, M. P. Cohen, and K. Baum		8. CONTRACT OR GRANT NUMBER(s): N00014-78-C-0147
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Fluorochem, Inc. 680 S. Ayon Ave. Azusa, CA 91702		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 659-796/10-26-84 (430)
11. CONTROLLING OFFICE NAME AND ADDRESS: Department of the Navy Office of Naval Research, Code 432 Arlington, VA 22217		12. REPORT DATE: February 1986 13. NUMBER OF PAGES: 61
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report): Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nitroheterocycles,
Nitrocyclobutanes,
Nitrations,
Fluoronitro polymers,
Fluoroazides,
Nuclear magnetic resonance spectra,
Infrared spectra,
Chromatography.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Fluoronitro polymers for use as binders in pyrotechnics applications were investigated. Isopropyl 3,3-difluroroacrylate and 2,2-difluorovinyl isopropyl ketone were synthesized from 3-chloro-3,3-difluoropropionate and 1-chloro-1,1-difluoro-4-methyl-3-pentanone. Attempted Michael addition reactions of nitronate ions to these olefins failed to give stable adducts. Reaction of 1-chloro-1,1-difluoro-4-methyl-3-pentanone with 2,2-dinitropropanol, 2,2-dinitro-2-fluoroethanol and 2,2,2-trifluoroethanol gave ethers 1,1-difluoro-1-(2,2-dinitropropoxy)-4-methyl-3-pentanone, 1,1-difluoro-1-(2,2-dinitro-2-fluoroethoxy)-4-methyl-3-pentanone and 1,1-difluoro-1-(2,2,2-trifluoroethoxy)-4-methyl-3-pentanone, respectively. Similar ethers were obtained from 3-chloro-3,3-difluoropropionate with these alcohols. The difunctional alcohol 2-fluoro-2-nitropropanediol gave the bis adduct with 1-chloro-1,1-difluoro-4-methyl-3-pentanone.

The geminal difluoroazides, 2-azido-2,2-difluoroacetophenone, 1-azido-1,1-difluoro-4-methyl-3-pentanone and isopropyl 3-azido-3,3-difluoropropionate were prepared from the corresponding chlorides with sodium azide. Reaction of lithium 2-nitropropane-1,3-diol acetonide with perfluoroalkyl iodides gave the corresponding 2-perfluoroalkyl-2-nitropropane-1,3-diacetonides.

Work was continued on the synthesis of polynitro derivatives of the furofuran ring system. The intermediate furans such as 5-nitro-2-methyl-3-furanmethanol acetate, 3-methyl-2-furanmethanol acetate, and 2,3-furandimethanol were synthesized, but closure of the second ring has not yet been effected.

Work was begun on the synthesis of 1,1,3,3-tetranitrocyclobutane. The model compound 1,1-dinitrocyclobutane was prepared from 1-nitrocyclobutane. Oxidation of 1,3-diaminocyclobutane gave 1,3-dinitrocyclobutane.

CONTENTS

I. INTRODUCTION

This report summarizes the research under Contract N00014-78-C-0147 during the period 1 January 1985 through 31 December 1985. The objective of this work is the synthesis of new high density, high energy compounds for explosives applications and fluoronitro polymers for binder applications. In the preceding report period,[1] several polynitro heterocyclic bicyclo[3.3.0]octanes were synthesized, and during the present period additional work was carried out extending this work to furo[3,2b]furan and furo[3,2b]pyrrole ring systems and polynitro derivatives of furans. In an extension of previous work on high energy small ring compounds such as trinitroazetidine,[1] nitro derivatives of cyclobutane were synthesized. Work was initiated during this period on synthetic routes to fluoronitro monomers for polymer application.

FLUORONITRO POLYMERS

Introduction.

The need exists for fluorinated polymers with nitro substituents for use as binders for pyrotechnics applications. Ideally, such a binder would contain a high percent by weight of fluorine, and no hydrogen. The binder should be stable thermally must be chemically compatible with a number of elemental metals. The processing requirements for the binder are not as critical as those for propellants; either castable systems or polymers suitable for compression molding are acceptable.

The most difficult requirement to meet from the standpoint of a chemical synthesis program is the absence of hydrogen. Hydrogen degrades the performance of flares. However, a binder would be useable with a

small amount of hydrogen, if it meets the other requirements.

Fluorocarbons as a class of compounds possess excellent chemical and thermal stability properties,[2] but there are certain limitations that must be considered when one extrapolates the chemistry of hydrocarbon-based nitropolymers. An important restriction is the instablility of compounds with OH or NH groups adjacent to CF groups; HF is eliminated.[3] Thus, a long-chain primary diol must have CH_2OH functionality. Groups containing CHF adjacent to CF_2 are only moderately stable and tend to eliminate HF. These effects can result in unstable polymers from stable monomers, as the following example illustrates.

$$\begin{matrix} R\text{-}CF_2\text{-}NCO \\ + \\ R'\text{-}CH_2OH \end{matrix} \longrightarrow R\text{-}CF_2\text{-}NH\text{-}CO\text{-}OCH_2\text{-}R' \longrightarrow R\text{-}CF{=}N\text{-}CO\text{-}OCH_2\text{-}R'$$

Based on the above criteria, the ideal monomer system would contain geminal dinitro functionality next to difluoro moieties, and these groupings would be isolated from the site of polymer formation functionality, such as isocyanate or acid halide, by a single methylene group. Thus, chemically stable systems with minimum hydrogen content could be obtained.

$$\text{---} CH_2\text{-}(CF_2)_x\text{-}C(NO_2)_2\text{-}(CF_2)_x\text{-}CH_2 \text{---}$$

Since 3,3-difluoroacrylic acid has been reported,[4] we examined the use of this material as a Michael acceptor with terminal dinitroalkanes. It was expected that 2,2-dinitro-1,3-propanediol in base functioning as an in-situ source of dinitromethane, would give 3,3,5,5-tetrafluoro-4,4-dinitropimelic acid. The Curtius reaction[5] would give 2,2,4,4-tetrafluoro-3,3-dinitropentanediisocyanate.

$$CF_2=CH-CO_2Et + HOCH_2C(NO_2)_2CH_2OH \xrightarrow{NaOH}$$

$$EtO_2CCH_2CF_2C(NO_2)_2CF_2CH_2CO_2Et \xrightarrow[2.\ SOCl_2]{1.\ HCl}$$

$$ClCOCH_2CF_2C(NO_2)_2CF_2CH_2COCl \xrightarrow{NaN_3}$$

$$OCNCH_2CF_2C(NO_2)_2CF_2CH_2NCO$$

In order to bring the total fluorine content of polyurethane or polyester systems based on the above components to the required 50%, an all fluorocarbon component must be used in partnership with one of the nitro-fluoro components. Perfluorocarboxylic acid esters tend to be hydrolytically labile, but CH_2CO_2R end groups are acceptable.

Preparation of 3,3-Difluoroacrylic acid derivatives.

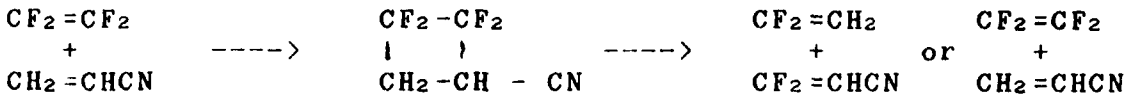
Although 2-fluoroacrylates[6] are well known, 3-fluoro[7] and 3,3-difluoro acrylic acid derivatives which contain no alpha fluorine are not readily available. Preparation of 3,3-difluoroacrylic acid from dehydrofluorination of 3,3,3-trifluoropropionic acid was reported,[4] but few experimental details other than observed pKa, were provided. Based on the hydrolytic instability of other 3,3-difluoroacrylic acid derivatives, the preparation of this acid in aqueous sodium hydroxide is questionable.

The esters of 3,3-difluoroacrylic acid, have been reported using a sequence beginning with the reation of iodine monochloride and 1,1,3,3,3-pentafluoropropene, followed by hydrolysis and finally, zinc reduction of the corresponding 2,3--dichloro-3,3-difluoropropionates.[8,9]

$$CF_3-CH=CF_2 + ICl \longrightarrow CF_3-CHI-CF_2Cl \longrightarrow$$

$$CF_3-CHI-COOH \longrightarrow CF_3-CHI-COOR \longrightarrow CF_2=CH-COOR$$

A more facile reported route[10] to 3,3-difluoroacryclic acid derivatives involves the cycloaddition reaction of acrylonitrile and tetrafluoroethylene followed by vacuum pyrolysis of the adduct. The [2 + 2] cycloaddition reaction gives 1-cyano-2,2,3,3-tetrafluorocyclobutane in 60% yield. This cyclobutane when heated at 700°C under vacuum undergoes a retro [2 + 2] reaction. Depending upon which bonds rupture, this reaction will give either the starting olefins, tetrafluoroethylene and acrylonitrile, or 1,1-difluoroethylene and 3,3-difluoroacrylonitrle. We repeated this reaction and observed no selectivity and the two possible acrylonitriles were formed in equal molar amounts.



Although 3,3-difluoroacrylonitrile was prepared by this pyrolysis, the yields were low, and the 50-50 mixture with the unfluorinated acrylonitrile could not be separated by distillation. Attempts to separate the mixture by free radical polymerization of acrylonitrile without reacting the fluorinated derivative were unsuccessful, although, some enrichment of 3,3-difluoroacrylonitrile in the mixture occured by this method when the mixture was allowed to stand for several months.

None of the existing routes to 3,3-difluoroacrylates gave these materials in sufficient quantity or purity for this investigation. This synthesis was accomplished, however, by Friedel-Crafts acylation of difluoroethylene to give 2-chloro-2,2-difluoroethyl alkyl ketones followed by regioselective Bayer-Villiger oxidation. Several workers[11,12] have shown that 1,1-difluoroethylene reacts under Friedel-Crafts conditions with acyl chlorides to give 2-chloro-2,2-difluoroethyl n-alkyl ketones. We found that isobutyryl chloride reacted similarily

with 1,1-difluoroethylene to give 1-chloro-1,1-difluoro-4-methyl-3-pentanone, in 40% yield.

$$CH_2{=}CF_2 + (CH_3)CH_2COCl \longrightarrow CF_2ClCH_2COCH(CH_3)_2$$

The reaction of acid chlorides with 1,1-difluoroethylene was catalyzed equally well with aluminium chloride or ferric chloride, but ferric chloride was the reagent of choice because of the ease of product isolation. The corresponding 2-chloro-2,2-difluoroethyl t-butyl ketone was prepared from 2,2-dimethylpropionyl chloride in poor yield. Benzoyl chloride and oxalyl chloride failed to give similar adducts.

Oxidation of 1-chloro-1,1-difluoro-4-methyl-3-pentanone with meta-chloroperbenzoic acid gave a 33% yield of isopropyl 3-chloro-3,3-difluoropropionoate. Although two oxidation products, isopropyl 3-chloro-3,3-difluoropropionoate and 2-chloro-2,2-difluoroethyl isobutyrate could conceivably be formed in this oxidation, only isopropyl 3-chloro-3,3-difluoropropionoate was observed. It is possible that a regiospecific oxidation occurred, but we did not rigorously rule out the possibility that only isopropyl 3-chloro-3,3-difluoropropionate survived the isolation techniques.

$$CF_2ClCH_2\overset{O}{\overset{\|}{C}}-CH(CH_3)_2 \xrightarrow{[O]} CF_2ClCH_2\overset{O}{\overset{\|}{C}}-O-CH(CH_3)_2 + ?\ \{(CH_3)_2CHC(O)OCH_2CF_2Cl\}$$

$$CF_2ClCH_2\overset{O}{\overset{\|}{C}}-CH(CH_3)_2 \xrightarrow{Et_3N} CF_2{=}CH-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2$$

$$CF_2ClCH_2\overset{O}{\overset{\|}{C}}-OCH(CH_3)_2 \xrightarrow{Et_3N} CF_2{=}CH-\overset{O}{\overset{\|}{C}}-O-CH(CH_3)_2$$

Dehydrochlorination of the ketone, 1-chloro-1,1-difluoro-4-methyl-3-pentanone, and the ester, isopropyl 3-chloro-3,3-difluoropropionoate, with triethylamine in diphenyl ether, gave 2,2-difluorovinyl isopropyl ketone and isopropyl 3,3-difluoroacrylate, respectively. These materials were isolated in 50% yield by distillation.

The beta fluorines in 2,2-difluorovinyl isopropyl ketone and isopropyl 3,3-difluoroacrylate were found to be unstable to hydrolysis. For example, dehydrohalogenation of 1-chloro-1,1-difluoro-4-methyl-3-pentanone, with solid sodium carbonate monohydrate gave only methyl isopropyl ketone. Presumably, the chlorodifluoro group was converted under these conditions to a beta-keto acid which subsequently decarboxylated to give the observed product.

$$CF_2ClCH_2COCH(CH_3)_2 \xrightarrow{Na_2CO_3(H_2O)} CF_2=CH-C(O)CH(CH_3)_2 \xrightarrow{H_2O}$$

$$HOOCCH_2C(O)CH(CH_3)_2 \longrightarrow CH_3C(O)CH(CH_3)_2 + CO_2$$

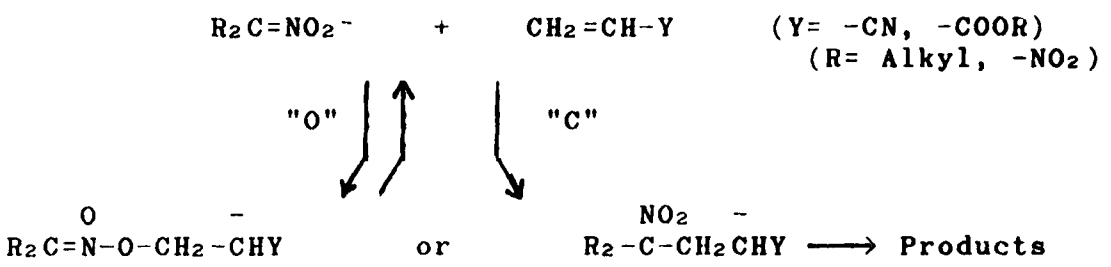
When 3,3-difluoroacrylonitrile was allowed to react with water, a similar reaction occurs with loss of organic fluorine and the formation of formyl acetonitrile.[10]

$$CF_2=CHCN + H_2O \longrightarrow HC(O)CH_2CN + F^-$$

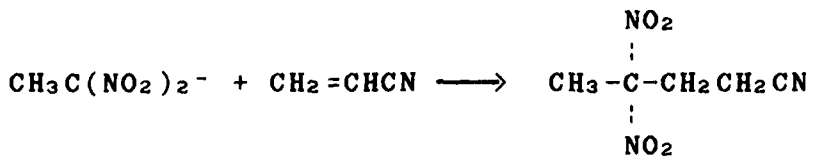
Michael Reactions of 3,3-difluoroacrylic Acid Derivatives.

The Michael addition of nitroalkane salts to a number of substituted and unsubstituted acrylic acid derivatives is well known. In the addition of an ambident nucleophile such as nitronate ion, to an activated olefin, addition can occur at either nucleophilic site.[13]

If the addition is irreversible, the product will be kinetically controlled and the product resulting from attack by the least hindered site will predominate. If the addition is reversible, as is usually the case, then the thermodynamically more stable product will result. When nitronate salts add to activated olefins, there is a rapid and usually reversible addition of the nitro group to the olefin at the oxygen of the nitro group. The slower, but irreversible, carbon addition leads to the isolatd product.



The reaction of acrylonitrile and the salt of 1,1-dinitroethane prepared in aqueous sodium hydride was reported to give the "C" adduct in 30% yield.[14] Since water is an unacceptable solvent for 3,3-difluoroacrylonitrile, we investigated the Michael addition of 1,1-dinitroethane and acrylonitrile in methanol - sodium methoxide and DMF - potassium fluoride.[15] The reaction was complete in several hours and 1-cyano-3,3-dinitrobutane, was isolated in 66% yield in methanol and 40% yield in DMF.



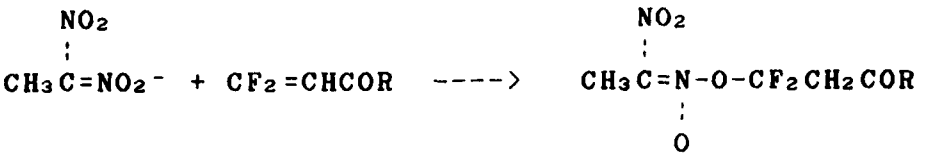
Reaction of the 50:50 mixture of acrylonitrile and 3,3-

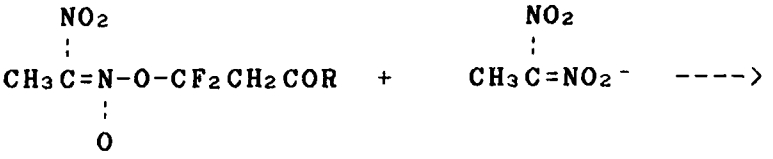
difluoroacrylonitrile, prepared from the vacuum pyrolysis of 1-cyano-2,2,3,3-tetrafluorocyclobutane, with anions of nitro alkanes was investigated. The acryonitrile component of this mixture reacted normally with 1,1-dinitroethane in methanol - sodium methoxide or DMF - potassium fluoride. However, no "C" - Michael additions to 3,3-difluoroacrylonitrile was observed. An almost immediate reaction was observed by ^{19}F NMR, but after aqueous work-up, no fluorine containing materials were isolated.

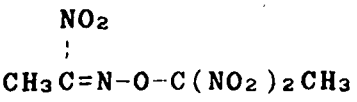
In the attempted reaction of 1,1-dinitroethane with the more hindered 3,3-bis(trifluoromethyl)acrylic acid, ^{19}F NMR analysis showed no reaction. However, in the case of 3,3-difluoroacrylonitrile, new ^{19}F NMR signals appeared between $\varnothing$ 10 and 20 ppm rather than in the expected region[16] of $\varnothing$ 80 - 120 ppm for "C" addition. These low field absorbances may be a result of the formation of an unstable "O" adduct of the nitro compound.

The attempted Michael reaction of 1,1-dinitroethane with 2,2-difluorovinyl isopropyl ketone and isopropyl 3,3-difluoroacrylate under a variety of conditions also failed to yield any evidence of "C" addition products of the nitro compound. In order to understand these reactions more clearly, the fate of the 1,1-dinitroethane was investigated. When the attempted Michael addition to 2,2-difluorovinyl isopropyl ketone was run in methylene chloride with the hindered base collidine, the 1,1-dinitroethane was converted in 85% yield to 2,5,5-trinitro-3-aza-4-oxa-2-hexene.

The formation of 2,5,5-trinitro-3-aza-4-oxa-2-hexene from the salt of 1,1-dinitroethane occurs spontaneously in the presence of amine catalysts, but proceeds slowly and in poor yield.[17,18] In the absence the 2,2-difluorovinyl ketone, the hexene is formed in only 15-20% yield







after 24 hours. The observed reaction in the presence of the ketone is similar to the reaction of the anion 1,1-dinitroethane with acetyl chloride in which reaction occurs exclusively "O" on the nitronate to give high yields of this hexene.[19]

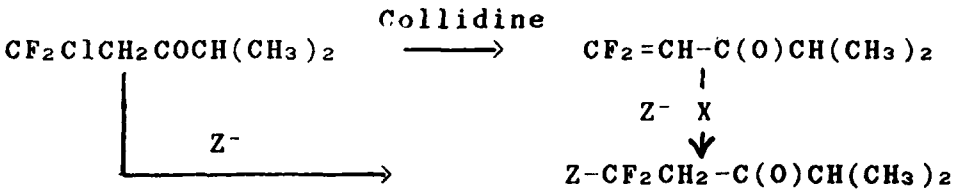
Thus, the isolation of 2,5,5-trinitro-3-aza-4-oxa-2-hexene from the reaction of the salt of 1,1-dinitroethane and 2,2-difluorovinyl isopropyl ketone indicates that Michael addition of the nitronate ion is occuring irreversibly by the "O" attack pathway. No evidence in this work has been obtained for any "C" Michael addition by anions of nitroalkanes to 3,3-difluorovinyl acrylic acid derivatives. Anions drived from nitro ethane as well as 1,1-dinitroethane and nitroform failed to give normal Michael adducts.

Displacement of Chloride from Chlorodifluoromethyl Groups.

It is generally considered that the chlorodifluoromethyl moiety is chemically inert under normal reaction conditions.[3] Indeed, a number of freons such as Freon 113 contain the chlorodifluoromethyl group and are used as common reaction solvents. Recently, however, there has been a

report of chloride displacement from Freon 113 by thiophenoxide ion.[20]

In the course of the study of the Michael additions to 3,3-difluoro acrylates, we found it convenient to generate these olefins in-situ from the 2-chloro-2,2-difluoroethyl precursers. As a result, adducts which are formally Michael adducts were produced by a route which appears to involve direct displacement of chloride from the chlorodifluoromethyl group.



Typically, the reaction of an alcohol and collidine in methylene chloride with 2-chloro-2,2-difluoroethyl isopropyl ketone or isopropyl 3-chloro-3,3-difluoropropionoate gave the corresponding ether. This method appears to be general, and ethers of trifluoroethanol, 2,2-dinitropropanol and 2-fluoro-2,2-dinitroethanol were prepared.

$CF_2ClCH_2COCH(Me)_2 + CF_3CH_2OH \longrightarrow Me_2CH-CO-CH_2-CF_2-O-CH_2CF_3$

" + $MeC(NO_2)_2CH_2OH \longrightarrow Me_2CH-CO-CH_2-CF_2-O-CH_2C(NO_2)_2Me$

" + $FC(NO_2)_2CH_2OH \longrightarrow Me_2CH-CO-CH_2-CF_2-O-CH_2C(NO_2)_2F$

$CF_2ClCH_2C(O)OCH(Me)_2 + CF_3CH_2OH \longrightarrow Me_2CHOC(O)CH_2CF_2-O-CH_2CF_3$

" + $MeC(NO_2)_2CH_2OH \longrightarrow Me_2CHOC(O)CH_2CF_2-O-CH_2C(NO_2)_2Me$

" + $FC(NO_2)_2CH_2OH \longrightarrow Me_2CHOC(O)CH_2CF_2-O-CH_2C(NO_2)_2F$

These reactions are especially of interest in light of the ease of deformylation of the nitro alcohols. For example, fluorodinitroethanol

reacts with acrylates or acrylonitrile under mild conditions to deformylate and give the corresponding "C" addition products, 3-fluoro-3,3-dinitrobutyrate and 3-fluoro-3,3-dinitrobutyronitrile, respectively. The "O" adducts were observed only when the Michael acceptor was an acetylenecarboxylate.[21]

$$FC(NO_2)_2-CH_2-OH + CH_2=CH-CN \longrightarrow FC(NO_2)_2-CH_2CH_2CN$$

$$" + HC\equiv C-COOR \longrightarrow FC(NO_2)_2-CH_2-O-CH=CHCOOR$$

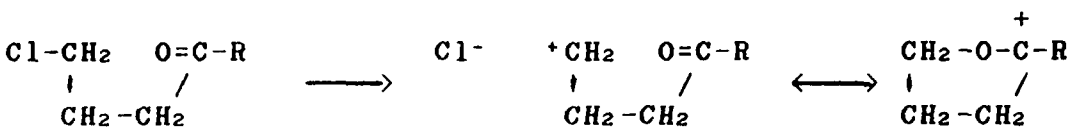
Reaction of difunctional alcohols with 2-chloro-2,2-difluoroethyl isopropyl ketone and isopropyl 3-chloro-3,3-difluoropropionate were also studied. However, 2,2-dinitro-1,3-propanediol (A-Diol) failed to give stable adducts, possibly because it deformylates readily[22] under very mild conditions leading to a nitronate ion, giving an unstable "O" adduct. Unlike A-Diol, the less easily deformylated 2-fluoro-2-nitro-1,3-propanediol reacted with 2-chloro-2,2-difluoroethyl isopropyl ketone to give the corresponding difunctional adduct 2,14-dimethyl-8-nitro-5,5,8,11,11-pentafluoro-6,10-dioxapentadecan-3,13-dione, which was isolated in 60% yield.

$$2\ CF_2ClCH_2COCH(CH_3)_2 + HOCH_2FC(NO_2)_2CH_2OH \longrightarrow$$

$$Me_2CH-CO-CH_2-CF_2-O-CH_2C(NO_2)FCH_2-O-CF_2CH_2-CO-CH(CH_3)_2$$

Under the reaction conditions used, dehydrohalogenation would not have occurred to produce the difluoroolefins. Several explanations are possible for the facile replacement of chloride ion in these reactions. Enhanced rates of displacement of bromide from bromodifluoromethyl by

phenoxide have been observed in the presence of enolizable ketones[23]. In the present case, enolization of the ketone to cause allylic activation of chloride towards Sn2 displacement, may explain the observed reaction, but this explanation of is unlikely to be valid in the corresponding ester since the enol content there is expected to be insignificant[24] (Reported enol content of ethyl acetate is 0%[25]). In nucleophilic substitution reactions beta to carbonyl groups in ketones or esters, the carbonyl groups generally do not have much effect on either Sn1 or Sn2 reaction rates[26] except through anchimeric assistance.[27] Such neighboring group participation has been observed in non-fluorinated omega substituted ketones which can form five or six membered rings.[28,29] In such systems, the solvolysis has a high Sn1 character indicating that the carbonyl is assisting solvolytic loss of the halide ion.



It is possible that in the case of these 2-chloro-2,2-difluoroethyl ketones and esters, the strong electron withdrawing effect of the geminal difluoro group increase the likelyhood of carbonyl participation sufficiently that resistance to four member ring formation is overcome. Kinetic studies would be required to elucidate this possibility.

Preparation of the Azidodifluoromethyl group.

The only example of an azido group attached to a carbon bearing two or more fluoro groups is the parent compound, azidotrifluoromethane.[30] This material is prepared by the reaction of nitrosotrifluoromethane with hydrazine followed by oxidation with chlorine. No examples of

displacement by azide ion on a carbon bearing a fluoro group have been reported.

$$CF_3NO + H_2N\text{-}NH_2 \xrightarrow{Cl_2} CF_3N_3$$

The facility of chloride displacement from 2-chloro-2,2-difluoroethyl isopropyl ketone and isopropyl 3-chloro-3,3-difluoropropionate by alcohols, suggests that other nucleophiles would react similarly. We found that sodium azide in acetone reacted with the chloro ketone and ester to give the corresponding azides. These fluoro azides were distilled without decomposition and were found to be quite stable to hydrolysis.

$$Me_2CH\text{-}CO\text{-}CH_2\text{-}CF_2\text{-}Cl + NaN_3 \longrightarrow Me_2CH\text{-}CO\text{-}CH_2\text{-}CF_2\text{-}N_3$$

$$Me_2CHO\text{-}CO\text{-}CH_2\text{-}CF_2\text{-}Cl + NaN_3 \longrightarrow Me_2CHO\text{-}CO\text{-}CH_2\text{-}CF_2\text{-}N_3$$

In an effort to elucidate the role of the beta carbonyl functionality in this reaction, other examples of this nucleophillic displacement of chloride from chlorodifluoro groups were sought. As expected, Freon 113 did not react with sodium azide, even under forcing conditions. However, although 1-chloro-1,1-difluoroacetophenone gave no reaction with sodium azide in refluxing acetone, at 100°C in diethylene glycol it gave the corresponding 1-azido-1,1-difluoroacetophenone, isolated by distillation in 81% yield. It therefore appears that the displacement of chloride ion from chlorodifluoromethyl groups may be more widely applicable to the synthesis of organofluoro compounds.

$$C_6H_5C(O)\text{-}CF_2\text{-}Cl + NaN_3 \longrightarrow C_6H_5C(O)\text{-}CF_2\text{-}N_3$$

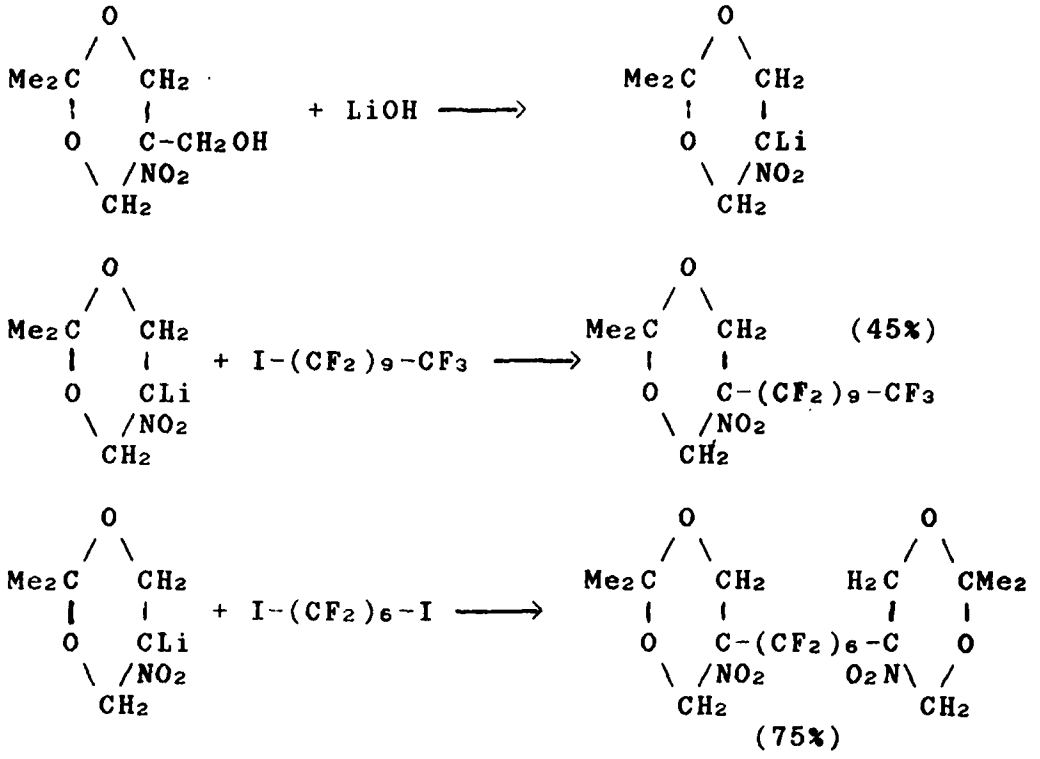
Radical Anion Coupling of Nitro Anions and Perfluoroalkyl Iodides.

In continuing the search for a general synthetic route to nitro group functionality next to geminal difluoro groups, we examined the radical anion coupling of nitro anions with perfluoroalkyl iodides. The reaction of the lithium salt of 2-nitropropane and perfluoroalkyl iodides has been reported to yield C-perfluoroalkylated nitro compounds.[31]

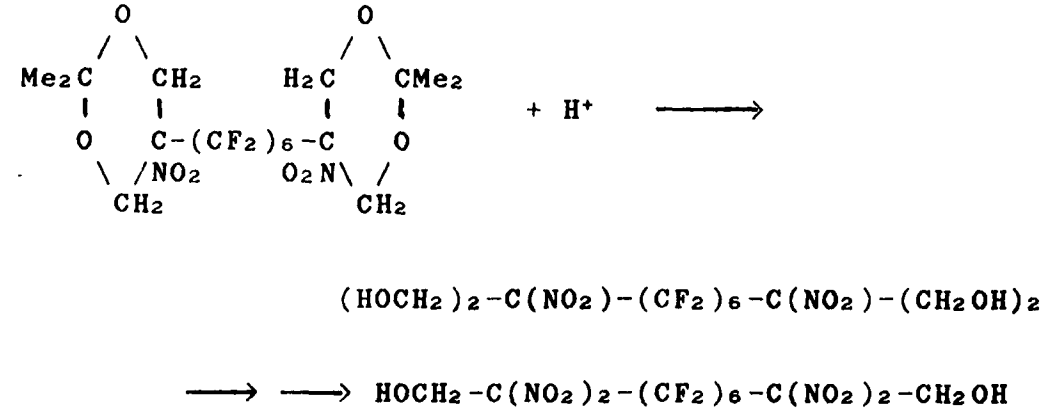
$$Me_2C{=}NO_2^- + CF_3(CF_2)_x{-}I \longrightarrow CF_3(CF_2)_x{-}\underset{\displaystyle NO_2}{\overset{\displaystyle |}{C}}{-}Me_2$$

Although this coupling to give perfluoroalkylated nitro compounds proceeds in high yield, it is appearently limited to the anions of secondary mononitro alkanes. Attempts to apply this reaction to dinitro alkanes such as salt of 1,1-dinitroethane failed. For this coupling reaction to be useful in preparing fluoronitro monomers, a method of functionallizing a methyl group next to nitro is needed. We, therefore, studied extensions of this reaction to a nitro ketal.

Reaction of tris(hydroxymethyl)nitromethane acetonide[32] with lithium hydroxide or tetra-n-butylammonium hydroxide using azeotropic removal of water by benzene gives the anhydrous salt of 1-nitro-4,4-dimethyl-3,5-dioxacyclohexane. The resulting nitronate salt was found to react with perfluoroalkyl iodides in dimethylacetamide under mild photochemical conditions to give perfluoroalkyl substituted nitro compounds.



Study of the hydrolysis of these perfluoroalkyl nitro acetonides to the corresponding nitro diols is under way. Deformylation and oxidative nitration of the nitrodiols should lead to geminal dinitro moities next to geminal difluoro groups. Applying this reaction sequence to the bis coupled products followed by formylation would give the useful tetranitro diol derivatives of perfluoroalkanes.



B. Experimental Section

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Spang Laboratories, Eagle Harbor, MI. Proton and fluorine NMR specta were recorded on a Varian T-60 spectrometer and the chemical shifts are reported in parts per million downfield from tetramethylsilane or chlorotrifluoromethane. Infrared spectra were recorded with a Perkin-Elmer 700 spectrometer.

1-Cyano-2,2,3,3-tetrafluorocyclobutane. A 1 L pipe bomb was charged with 125 g (215 mL, 4.0 mol) of acrylonitrile, cooled with liquid nitrogen, and 80 g (0.8 mol) of tetrafluoroethylene was added. The bomb was sealed and heated for 16 h at 150°C. The resulting mixture was distilled through a 18" vigreux column to give, after a 80 g of forerun of acrylonitrile (bp 80-84°C), 79 g (60% based on tetrafluoroethylene) of 1-cyano-2,2,3,3-tetrafluorocyclobutane, bp 148-150°C (lit bp 150°C[10]): ^{1}H NMR ($CDCl_3$) δ 2.9 (m, 2 H), 3.4 (m, 2 H); ^{19}F NMR (Freon 113) ϕ 112, 116, 120, 124, 126 (m, 2:4:2:3:1) ppm.

3,3-Difluoroacrylonitrile - Acrylonitrile Mixture. Flash vacuum pyrolysis apparatus was constructed from a 3 cm x 35 cm quartz tube sealed at one end and placed in a vertical tube furnace. The tube was half-filled with silica sand and fitted with pressure equalizing dropping funnel. The top of the funnel was connected to sequential liquid nitrogen-ethanol (-110°C) and liquid nitrogen traps to a 10 mm vacuum source. In a typical run, the tube furnace was heated to 750°C and 52 g (0.5 mol) of 1-cyano-2,2,3,3-tetrafluorocyclobutane was added at a rate of 1 drop each 4 sec. Upon completion of the addition, the mixture collected in the first trap (28 g) was distilled to give two fractions, 16.5 g of a mixture of 3,3-difluoroacrylonitrile - acrylonitrile (equal molar), bp 84-

86°C and 11.5 g (bp 140-145°C) of unreacted starting material. The mixture of acrylonitriles could not be separated by distillation. Upon standing for several months, the mixture slowly became enriched in 3,3-difluoroacrylonitrile as acrylonitrile formed a solid polymer that could be removed by filtration. No analytically pure 3,3-difluoroacrylonitrile could be obtained by this procedure. Spectra were recorded for the 50-50% mole mixture of 3,3-difluoroacrylonitrile and acrylonitrile: ^{1}H NMR ($CDCl_3$) δ 4.3 (d, J = 24 Hz), 5.5 (m, 3 H); ^{19}F NMR (Freon 113) ø 64.4 (d of d, J = 24 and 16 Hz, 1 F), 68.0 (d, J = 16 Hz, 1 F) ppm.

1-Chloro-1,1-difluoro-4-methyl-3-pentanone. A mixture of 200 g (1.25 mol) of anhydrous ferric chloride in 1 L of methylene chloride was cooled to -10°C, and while being continuously saturated with 1,1-difluoroethylene, was treated dropwise with 106 g (1.0 mol) of isobutyryl chloride. After the addition was complete, the flow of 1,1-difluoroethylene was continued for 10 min, the mixture stirred for 1 h at 0°C, and poured onto a mixture of 500 g of ice and 200 mL of 35% aqueous hydrochloric acid. The organic layer was separated, washed with 2 x 200 mL cold 10% aqueous hydrochloric acid, and dried over magnesium sulfate, and the solvent was removed in vacuo. The residual oil was distilled at 65-75°C (10 mm) to yield a liquid which contained about 30% non-fluorine containing impurities by nmr analysis. Redistillation twice gave 70 g (41%) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone, bp 68-70 (25 mm): IR (CH_2Cl_2) 3050 (C-H), 1710 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (d, J = 7 Hz, 6 H), 2.7 (m, J= 7 Hz, 1 H), 3.5 (t, J= 12 Hz, 2 H); ^{19}F NMR (Freon 113) ø 57.0 (t, J= 12 Hz) ppm.

Anal. Calcd for $C_6H_9ClF_2O$: C, 42.24; H, 5.30; F, 22.27. Found: C, 42.12; H, 5.51; F, 22.05.

Isopropyl 3-Chloro-3,3-difluoropropionate. A solution of 7.5 g

(0.05 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone and 10 g of m-chloroperbenzoic acid in 50 mL of 1,2-dichloroethane was heated at 60°C for 16 h. The solution was cooled, filtered, and washed with 5% aqueous sodium carbonate solution. The organic layer was dried over magnesium sulfate and distilled to yield 3.0 g (33%) of isopropyl 3-chloro-3,3-difluoropropionate, bp 68-70°C (10 mm): IR (CH_2Cl_2) 3000 (C-H), 1745 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J= 7 Hz, 6 H), 3.0 (t, J = 12 Hz, 2 H), 4.8 (m, 1 H); ^{19}F NMR ∅ 58.0 (t, J= 12 Hz) ppm.

Anal. Calcd for $C_6H_9ClF_2O_2$: C, 38.62; H, 4.86; F, 20.36. Found: C, 38.75; H, 4.80; F, 20.10.

Isopropyl 3,3-Difluoroacrylate. A solution of 5.5 g (0.03 mol) of isopropyl 3-chloro-3,3-difluoropropionate and 3.0 g (0.03 mol) of triethylamine in 50 mL of methylene chloride was stirred 30 min at 25°C. This solution was washed with 20 mL of cold 10% aqueous hydrochloric acid, dried over magnesium sulfate and solvent was evaporated to give an oil which was distilled to yield 2.2 g (49%) of isopropyl 3,3-difluoroacrylate, bp 43-45 (10 mm): IR (CH_2Cl_2) 3000 (C-H), 1745 (C=O) cm^{-1}; ^1H NMR (CCl_3) δ 1.05 (d, J= 7 Hz, 6 H), 4.7 (m, 1 H), 4.8 (m, 1 H); ^{19}F NMR (Freon 113) ∅ 63.5 (ABXq, J= 3, 14 Hz, 1 F), 58.0 (ABX q, J= 14, 22 Hz, 1 F) ppm.

Anal. Calcd for $C_6H_8F_2O_2$: C, 48.00; H, 5.36. Found: C, 47.91; H, 5.33.

1,1-Difluoro-4-methyl-1-penten-3-one. A solution of 3.7 g (0.02 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone in 20 mL of diphenyl ether was cooled to 10°C and treated dropwise with 2.2 g (0.02 mol) of triethylamine. The resulting mixture was heated to 105°C under vacuum (20 mm) and the liquid which distilled was collected and redistilled to

yield 1.5 (55%) of 1,1-difluoro-4-methyl-1-penten-3-one, bp 40-42 (20 mm): IR (CH_2Cl_2) 3000 (C-H), 1705 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 7 Hz, 6 H), 2.5 (m, 1 H), 5.2 (ABXq, J= 3, 22 Hz, 1 H); ^{19}F NMR ($CDCl_3$) ϕ 64.2 (ABXq, J= 3, 14 Hz, 1 F), 59 (ABXq, J= 14, 22 Hz, 1 F) ppm.

Anal. Calcd for $C_6H_8F_2O$: C, 53.73; H, 5.96. Found: C, 53.73; H, 5.73.

Reaction of 1-Chloro-1,1-difluoro-4-methyl-3-pentanone with Sodium Carbonate. A mixture of 3.6 g (0.02 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone and 8 g of sodium carbonate monohydrate, was stirred at 50°C for 16 h. The residue was distilled to give 1.3 g (76%) of methyl isopropyl ketone, bp 40-42 (20 mm), identified by IR and NMR comparison with authentic material.

1-Cyano-3,3-dinitrobutane[14]. Procedure A. To a solution of 1.2 g (0.01 mol) of 1,1-dinitroethane and 0.5 g (0.005 mol) of sodium methoxide in 20 mL of methanol was added 0.53 g (0.01 mol) of acrylonitrile and the mixture was stirred at 20°C for 18 h at which time NMR analysis of an aliquot showed starting acrylonitrile to be totally consumed. The mixture was added to 20 mL of aqueous hydrochloric acid, the methanol evaporated in vacuo and the water layer extracted with 20 mL of methylene chloride. The organic layer was separated, dried over magnesium sulfate, evaporated and distilled to give 1.1 g (64%) of 1-cyano-3,3-dinitrobutane, bp 125-128°C (0.5 mm) (lit. bp 125-127°C (1 mm)[14])

Procedure B. To a solution of 1.2 g (0.01 mol) of 1,1-dinitroethane and 0.53 g (0.01 mol) of acrylonitrile in 10 mL of DMF was added 0.05 g of anhydrous potassium fluoride, and the mixture was stirred at 20°C for 18 h at which time NMR analysis of an aliquot showed starting materials to be unreacted. The mixture was then heated to 80°C for 2 h, cooled and

added to 20 mL of water. The mixture was extracted with 20 mL of methylene chloride and the organic layer dried over magnesium sulfate, evaporated and the residual oil distilled to give 0.75 g (44%) of 1-cyano-3,3-dinitrobutane, bp 126-128°C (0.5 mm).

Attempted Reaction of 1,1-Dinitroethane with 3,3-Bis(trifluoromethyl)acrylic acid. To a solution of 1.2 g (0.01 mol) of 1,1-dinitroethane and 2.08 g (0.01 mol) of 3,3-bis(trifluoromethyl)acrylic acid in 10 mL of DMF was added 0.05 g of anhydrous potassium fluoride, and the mixture was stirred at 80°C for 2 weeks. Periodic NMR analysis of aliquots showed that the starting materials were unreacted.

Attempted Reaction of 1,1-Dinitroethane with 3,3-Difluoroacrylonitrile To a solution of 6.0 g (0.05 mol) of 1,1-dinitroethane and 2.0 g (0.02 mol) of sodium methoxide in 20 mL of methanol was added 3.8 g (approximately 0.05 mol) of a 50%-50% mixture of 3,3-difluoroacrylonitrile and acrylonitrile and the mixture was stirred at 20°C for 18 h at which time NMR analysis of an aliquot showed starting acrylonitrile to be totally consumed. The mixture was added to 20 mL of aqueous hydrochloric acid, the methanol evaporated in vacuo and the water layer extracted with 20 mL of methylene chloride. The organic layer was separated, dried over magnesium sulfate, stripped of solvent and distilled to give 3.0 g (50%) of 1,1-dinitroethane, bp 85-90 (0.5mm) and 3.0 g (60%) of 1-cyano-3,3-dinitrobutane, bp 125-128°C (0.5 mm). No fluorine containing materials were distilled or remained in the pot residue.

To a solution of 1.2 g (0.01 mol) of 1,1-dinitroethane and 0.5 g of a 50%-50% mixture of 3,3-difluoroacrylonitrile and acrylonitrile in 10 mL of DMF was added 0.05 g of anhydrous potassium

fluoride, and the mixture was stirred at 80°C for 2 h, cooled and added to 20 mL of water. The mixture was extracted with 20 mL of methylene chloride and the organic layer was separated, dried over magnesium sulfate, and solvent was evaporated. The residual oil was found to have no organic fluorine containing materials by ^{19}F NMR analysis.

Reaction of 1,1-difluoro-4-methyl-1-penten-3-one with 1,1-Dinitroethane. A mixture of 0.65 g (0.005 mol) of 1,1-difluoro-4-methyl-1-penten-3-one and 0.60 g (0.005 mol) of 1,1-dinitroethane in 10 mL of methylene chloride was cooled to 15°C in a water bath and 0.2 g of collidine was added. After several minutes a gas evolved. The mixture was stirred at 20°C for 16 h, washed with 10 mL of 10% aqueous hydrochloric acid, dried over magnesium sulfate and the methylene chloride was evaporated in vacuo. The residual oil was crystallized from ethanol to give 0.48 g (85%) of 2,5,5-trinitro-3-aza-4-oxa-2-hexene, mp 114-115 (lit. mp 117-120[17,18]). No organic fluorine-containing materials were observed in the crude oil by ^{19}F NMR analysis.

Attempted Reaction of 1,1-Difluoro-4-methyl-1-penten-3-one and Cyclopentadiene.. A solution of 1.0 g (0.0062 mol) of 1,1-difluoro-4-methyl-1-penten-3-one and 0.4 g (0.0062 mol) of cyclopentadiene in 10 mL of methylene chloride were stirred at 20°C for 1 h during which time the solution became cloudy and ^{19}F NMR analysis showed the starting material was reacted. Upon standing 16 h at 20°C, the solution became a tarry black jelly from which no non-polymeric materials could be isolated.

1,1-Difluoro-1-(2,2,2-trifluoroethoxy)-4-methyl-3-pentanone. A solution of 3.6 g (0.02 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone, 6.5 g (0.06 mol) of 2,2,2-trifluoroethanol and 2.8 g (0.023 mol) of collidine in 50 mL of methylene chloride was stirred at 25°C for 16 H at which time ^{19}F NMR showed the starting ketone was completely

consumed. The solution was washed with 2 x 50 mL of 10% aqueous hydrochloric acid, dried over magnesium sulfate and distilled to yield 3.3 g (71%) of 1,1-difluoro-1-(2,2,2-trifluoroethoxy)-4-methyl-3-pentanone, bp 55-57°C (3 mm): IR (CH_2Cl_2): 3000 (C-H), 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (d, J= 7 Hz, 6 H), 2.5 (septet, J= 7 Hz, 1 H), 3.0 (t, J= 8 Hz, 2 H), 3.95 (q, J= 8, 2 H); ^{19}F NMR ($CDCl_3$) ϕ 71.6 (t, J=8 Hz, 2 F), 74.8 (t, J= 8 Hz, 3 F) ppm.

Anal. Calcd for $C_8H_{11}F_5O_2$: C, 41.03; H, 4.73; F, 40.57. Found: C, 41.05; H, 4.90; F, 40.68.

1,1-Difluoro-1-(2,2-dinitropropoxy)-4-methyl-3-pentanone. A solution of 1.7 g (0.01 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone, 3.0 g (0.02 mol) of 2,2-dinitropropanol and 1.2 g (0.01 mol) of collidine in 50 mL of methylene chloride was stirred at 25°C for 2 h at which time ^{19}F NMR showed the starting ketone was completely consumed. The solution was washed with 2 x 50 mL of 10% aqueous hydrochloric acid, and 2 x 25 mL 5% aqueous sodium carbonate, dried over magnesium sulfate and distilled to yield 2.6 g (92%) of 1,1-difluoro-1-(2,2-dinitropropoxy)-4-methyl-3-pentanone, bp 110-112 °C (0.5 mm): IR (CH_2Cl_2) 3000 (C-H), 1710 (C=O), 1570, 1450 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J=7 Hz, 6 H), 2.2 (s, 3 H), 2.55 (septet, J= 7 Hz, 1 H), 3.2 (t, J= 9 Hz, 2 H), 4.6 (s, 2 H); ^{19}F NMR ($CDCl_3$) ϕ 71.0 (t, J= 9 Hz) ppm.

Anal. Calcd for $C_9H_{14}N_2F_2O_6$: C, 38.03; H, 4.96; N, 9.95; F, 13.36. Found: C, 38.16; H, 4.96; N, 9.91; F, 13.37.

1,1-Difluoro-1-(2,2-dinitro-2-fluoroethoxy)-4-methyl-3-pentanone. A solution of 3.4 g (0.02 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone, 3.0 g (0.02 mol) of 2,2-dinitro-2-fluoroethanol and 2.8 g (0.023 mol) of collidine in 50 mL of methylene chloride was stirred at

25°C for 48 h at which time ^{19}F NMR showed the starting ketone was completely consumed. The solution was washed with 2 x 50 mL of 10% aqueous hydrochloric acid, dried over magnesium sulfate and distilled to give 2.4 g (83%) of 1,1-difluoro-1-(2,2-dinitro-2-fluoroethoxy)-4-methyl-pentanone, bp 104-106°C (0.5 mm): IR (CH_2Cl_2): 3000 (C-H), 1710 (C=O), 1550, 1460 (NO_2)cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J=7 Hz, 6 H), 2.55 (septet, J= 7 Hz, 1 H), 3.2 (t, J= 14 Hz, 2 H), 4.9 (s, 1 H), 5.1 (d, J=2, 1 H); ^{19}F NMR ($CDCl_3$) ∅ 71.0 (t, J= 14, 2 F), 107.0 (triplet of doublets J= 9, 2 Hz, 1 F) ppm.

Anal. Calcd for $C_8H_{11}N_2F_3O_6$: C, 33.34; H, 3.85; N, 9.72; F, 19.78. Found: C, 33.46; H, 3.81; N, 9.81; F, 19.62.

Isopropyl 3,3-Difluoro-3-(2,2-dinitropropoxy)propionate. A solution of 1.8 g (0.01 mol) of isopropyl 3-chloro-3,3-difluoropropionate, 3.0 g (0.02 mol) of 2,2-dinitropropanol and 1.0 g (0.01 mol) of triethylamine in 50 mL of methylene chloride was stirred at 25°C for 16 H at which time ^{19}F NMR showed the starting ketone was completely consumed. The solution was washed with 2 x 50 mL of 10% aqueous hydrochloric acid, and 2 x 25 mL 5% aqueous sodium carbonate, dried over magnesium sulfate and distilled to give 0.98g (33%) of isopropyl 3,3-difluoro-3-(2,2-dinitropropoxy)-propionate, bp 125-128°C (1.0 mm): IR (CH_2Cl_2) 3000 (C-H), 1750 (C=O), 1575, 1450 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (d, J=7 Hz, 6 H), 2.1 (s, 3 H), 3.0 (t, J= 10 Hz, 2 H), 4.8 (s, 2 H), 5.0 (septet, J= 7 Hz, 1 H); ^{19}F NMR ($CDCl_3$) ∅ 78.0 (t, J= 10 Hz) ppm.

Anal. Calcd for $C_9H_{14}N_2F_2O_7$: C, 36.00; H, 4.70; N, 9.30; F, 12.66. Found: C, 35.89; H, 4.62; N, 9.44; F, 12.70.

Isopropyl 3,3-difluoro-3-(2,2-dinitro-2-fluoroethoxy)propionate. A solution of 1.8 g (0.01 mol) of isopropyl 3-chloro-3,3-difluoropropionate, 1.5 g (0.01 mol) of 2,2-dinitro-2-fluoroethanol and

1.2 g (0.01 mol) of collidine in 20 mL of methylene chloride was stirred at 25°C for 24 h at which time ^{19}F NMR showed the starting ketone was completely consumed. The solution was washed with 2 x 50 mL of 10% aqueous hydrochloric acid, dried over magnesium sulfate and distilled to give 1.6 g (53%) of isopropyl 3,3-difluoro-3-(2,2-dinitro-2-fluoroethoxy)propionate, bp 98-100°C (1 mm): IR (CH_2Cl_2) 3000 (C-H), 1760 (C=O), 1550, 1460 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 7 Hz, 6 H), , 3.2 (t, J = 10 Hz, 2 H), 4.9 (s, 1 H), 5.1 (d, J = 2, 1 H), 5.1 (septet, J = 7 Hz, 1 H); ^{19}F NMR ϕ 71.0 (t, J = 10, 2 F), 106.0 (triplet of doublets J = 9, 2 Hz, 1 F) ppm.

Anal. Calcd for $C_8H_{11}N_2F_3O_7$: C, 31.58; H, 3.65; N, 9.12. Found: C, 31.40; H, 3.80; N, 9.32.

2,14-Dimethyl-8-nitro-5,5,8,11,11-pentafluoro-6,10-dioxapentadeca-3,13-dione. A solution of 4.0 g (0.022 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone, 1.4 g (0.01 mol) of 2-nitro-2-fluoropropane-1,3-diol and 2.4 g (0.02 mol) of collidine in 25 mL of methylene chloride was stirred at 25°C for 24 H at which time ^{19}F NMR showed the starting ketone was completely consumed. The solution was washed with 2 x 50 mL of 10% aqueous hydrochloric acid, and dried over magnesium sulfate to yield 3.4 g (85%) of crude 2,14-dimethyl-8-nitro-5,5,8,11,11-pentafluoro-6,10-dioxapentadeca-3,13-dione as an oil which was essentially pure by NMR analysis. An analytical sample was prepared by chromatographing the crude oil on silica gel with hexane containing 5% ethyl acetate. Attempted distillation of the oil at 130°C (0.1 mm) failed to yield any material. IR (CH_2Cl_2) 3000 (C-H), 1720 (C=O), 1580, 1460 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (d, J = 7 Hz, 12 H), 2.5 (septet, J = 7 Hz, 2 H), 3.0 (t, J = 10 Hz, 4 H), 4.3 (d, J = 16 Hz, 4 H); ^{19}F NMR ($CDCl_3$) ϕ 71.0 (t,

J = 10, 4 F), 133.6 (quint, J = 16 Hz, 1 F) ppm.

Anal. Calcd for $C_{15}H_{22}NF_5O_6$: C, 44.23; H, 5.58; N, 3.63. Found: C, 44.29; H, 5.67; N, 3.63.

Attempted Reaction of 1-Chloro-1,1-difluoro-4-methyl-3-pentanone with 2,2-Dinitropropane-1,3-diol. A solution of 4.0 g (0.022 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone, 1.7 g (0.01 mol) of 2,2-nitropropane-1,3-diol and 2.4 g (0.02 mol) of collidine in 25 mL of methylene chloride was stirred at 25°C for 24 H at which time ^{19}F NMR showed the starting ketone was completely consumed. The solution was washed with 2 x 50 mL of 10% aqueous hydrochloric acid, dried over magnesium sulfate and evaporated to yield less than 0.3 g of a residual which contained no organic material containing fluorine functionality an shown by ^{19}F NMR analysis.

Attempted Reaction of 1-Chloro-1,1-difluoro-4-methyl-3-pentanone with Sodium Nitrite. A solution of 3.6 g (0.02 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone and 1.4 g (0.02 mol) of sodium nitrite was stirred in 20 mL of acetonitrile at 25°C. Analysis of the reaction mixture after 4 weeks by ^1H and ^{19}F NMR showed the 1-chloro-1,1-difluoro-4-methyl-3-pentanone to be unchanged.

2-Azido-2,2-difluoroacetophenone. A mixture of 1.8 g (0.01 mol) of chlorodifluoroacetophenone and 1.0 g (0.014 mol) of sodium azide in 5 mL of dimethyl sulfoxide was heated at 100°C for 5 min and then cooled to ambient temperature. After the addition of 50 mL of water, the mixture was extracted with 20 mL of methylene chloride, and the organic layer washed with 2 x 20 mL of water, dried with magnesium sulfate and distilled to give 1.5 g (81%) of 2-azido-2,2-difluoroacetophenone, bp 75-76 (1.0 mm): IR (CH_2Cl_2) 3050 (C-H), 2200 ($-N_3$), 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0-7.5(m); ^{19}F NMR ($CDCl_3$) ϕ 78.4 (s) ppm.

Anal. Calcd for $C_6H_5F_2N_3O$: C, 48.74; H, 2.56; N, 21.31. Found: C, 48.67; H, 2.81; N, 21.02.

1-Azido-1,1-difluoro-4-methyl-3-pentanone. A mixture of 1.7 g (0.01 mol) of 1-chloro-1,1-difluoro-4-methyl-3-pentanone and 0.8 g (0.011 mol) of sodium azide in 10 mL of acetone was stirred at 25°C for 1 h at which time ^{19}F NMR analysis showed the reaction to be complete. The solvent was evaporated in vacuo and the residue distilled to yield 1.2 g (67%) of 1-azido-1,1-difluoro-4-methyl-3-pentanone, bp 30-31 (0.5 mm): IR (CH_2Cl_2) 3000 (C-H), 2190 ($-N_3$), 1710(C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (d, J= 7 Hz, 6 H), 2.6 (septet, J = 7 Hz, 1 H), 3.1 (t, J= 11 Hz, 2 H); ^{19}F NMR ($CDCl_3$) ϕ 70.4 (t, J= 11 Hz) ppm.

Anal. Calcd for $C_6H_9F_2N_3O$: C, 40.67; H, 5.12; N, 23.70. Found: C, 40.57; H, 5.01; N, 23.65.

Isopropyl 3-Azido-3,3-difluoropropionate. A mixture of 2.0 g (0.011 mol) of isopropyl 3-chloro-3,3-difluoropropionate and 1.2 g (0.017 mol) of sodium azide in 10 mL of acetone was stirred at 25°C for 16 h at which time ^{19}F NMR analysis showed the reaction to be complete. The solvent was evaporated in vacuo and the residue distilled to yield 1.1 g (53%) of isopropyl 3-azido-3,3-difluoropropionate, bp 55-58 (20 mm): IR (CH_2Cl_2) 3000 (C-H), 2190 ($-N_3$), 1760 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, J= 7 Hz, 6 H), 3.0 (t, J = 12 Hz, 2 H), 5.05 (septet, J = 7 Hz, 1 H); ^{19}F NMR ($CDCl_3$) ϕ 70.4 (t, J= 12 Hz) ppm.

Anal. Calcd for $C_6H_9F_2N_3O_2$: C, 37.30; H, 4.69; N, 21.75. Found: C, 37.09; H, 4.87; N, 22.06.

Preparation of Lithium 2-Nitropropane-1,3-diol Acetonide. A mixture of 9.5 g (0.05 mol) of 2-hydroxymethyl-2-nitropropane-1,3-diol monoacetonide and 2.1 g (0.05 mol) of lithium hydroxide monohydrate were

suspended in 50 mL of benzene was refluxed under nitrogen and water removed azetropically in a Dean-Stark trap. When no more water azetrope was formed, the solvent was removed on a rotary evaporator and 20 mL of DMF was added to dissolve the resultant pale yellow salt. This solution was used immediately.

2-(Perfluorodecyl)-2-nitropropane-1,3-diol Acetonide. A solution of 0.05 mol of lithium 2-nitropropane-1,3-diol acetonide in 20 mL of DMF was added to a solution of 6.5 g (0.01 mol) of perfluorodecyl iodide in 30 mL of DMF under nitrogen and the mixture was stirred at 25°C in laboratory light. After 24 h, ^{19}F NMR analysis of the reaction mixture showed the absence of the reactant perfluorodecyl iodide. The mixture was poured into 200 mL of water, and the solid which formed was filtered, washed with 2 x 100 mL water, dried in vacuo and sublimed to give 5.1 g (74%) of 2-(perfluorodecyl)-2-nitropropane-1,3-diol acetonide, mp 65-68°C: IR (CH_2Cl_2) 3000 (C-H), 1570, (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (s, 3 H), 1.4 (s, 3 H), 4.25 and 4.7 (AB d, J = 13 Hz, 4 H); ^{19}F NMR ($CDCl_3$) ϕ 81.2 (m, 3 F), 118.4 (m, 16 F), 122.8 (m, 2 F) ppm.

Anal. Calcd for $C_{16}H_{10}NF_{21}O_4$: C, 27.72; H, 1.40; N, 2.00. Found: C, 27.84; H, 1.54; N, 2.05.

2,9-Bis(hydroxymethyl)-2,9-dinitro-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane-1,10-diol Diacetonide. A solution of 0.05 mol of lithium 2-nitropropane-1,3-diol acetonide in 20 mL of DMF was added to a solution of 5.6 g (0.01 mol) of 1,6-perfluorohexyl diiodide in 100 mL of DMF under argon and the mixture stirred at 25°C in a pyrex flask in direct sunlight. After several minutes solids began to form. The reaction mixture was monitored by ^{19}F NMR and stirred until all the starting perfluoro diiodide was consumed (from 1 h to 2 days). The mixture was poured into 300 mL of water, filtered, and washed with 2 x

100 mL of water. The residual solids were dissolved in 80 mL of methylene chloride, and dried over magnesium sulfate. The solvent was evaporated and the solid was recrystallized from acetone to give 5.0 g (90%) of 2,9-bis(hydroxymethyl)-2,9-dinitro-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane-1,10-diol diacetonide, mp 138-139°C: IR (CH_2Cl_2) 3000 (C-H), 1565 (NO_2), 1350, 1210, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (s, 3 H), 1.4 (s, 3 H), 4.25 and 4.7 (Assym AB, J= 13 Hz, 4 H), ^{19}F NMR ($CDCl_3$) ϕ 113.2 (m, 2 F), 117.2 (m, 2 F), 118.8 (m, 2 F) ppm.

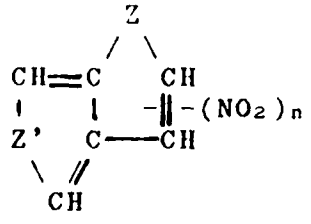
Anal. Calcd for $C_{18}H_{20}N_2F_{12}O_4$: C, 34.80; H, 3.25; N, 4.50. Found: C, 34.54; H, 3.20; N, 4.41.

III. HETEROCYCLIC POLYNITRO COMPOUNDS

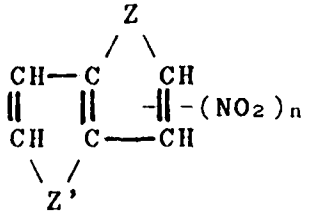
A. DISCUSSION.

Introduction.

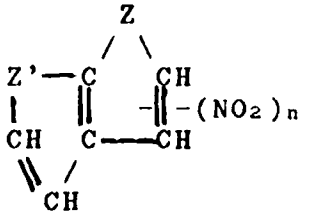
A study of the synthesis of polycyclic nitro compounds was continued with the objective of producting useful high density explosives. In the preceeding report period[1], several nitro derivatives of the saturated heterocyclic system bicyclo[3.3.0]-2,6-dioxaoctane were prepared. Based on calcuations of density, a number of polynitro unsaturated bicyclic heterocycles were selected as potential targets. Specifically these targets, shown below, are the structurally isomeric furo[2,3b]furan, furo[3,2b]furan, and furo[3,4b]furan (where Z = Z' = "O"); furo[2,3b]-pyrrole, furo[3,2b]pyrrole, and furo[3,4b]pyrrole (where Z = "O" and Z' = "N-H"); and pyrrolo[2,3b]pyrrole, pyrrolo[3,2b]pyrrole, and pyrrolo-[3,4b]pyrrole (where Z = Z' = "N-H"). No derivatives of any of these ring systems containing nitro groups have previously been reported.



[3,4b]



[3,2b]



[2,3b]

TABLE I
Calculated Densities of Target Bicycloheterocycles

	n = 2	n = 3	n = 4
Z = Z' = "O"	1.88	1.97	2.0+
Z = "O"; Z' = "N-H"	1.85	1.94	2.0
Z = Z' = "N-H"	1.83	1.91	1.97

Of particular interest as target compounds are the [3,4b] systems in which three nitro groups can be placed at the 2 and 5 positions of one ring and at either the 4 or 5 position of the the second without steric interaction. Introduction of a fourth nitro group into the system where Z = Z' = "O" to give a pernitrated material has the greatest likelyhood of giving a material stable to hydrolysis.

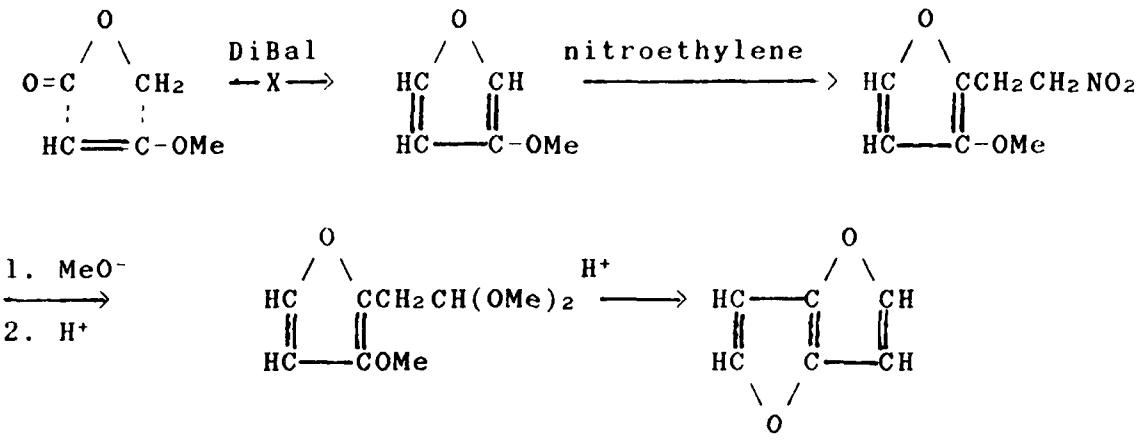
Aromatic stability calculations[33] for these target compounds indicate that derivatives of furo[2,3b]furan and furo[3,2b]furan should be more stabilized via resonance energy than furan itself, while furo[3,4b]furan will be somewhat less stable. Similar stabilities are predicted for the corresponding furopyrroles and the pyrrolopyrroles. Since furo[2,3b]furan contains an internal ketene acetal functionality, it was eliminated as a target compound due to the poor chemical stability of this class of compounds.

Attempted Synthesis of Polynitrofuro[3,2b]furan

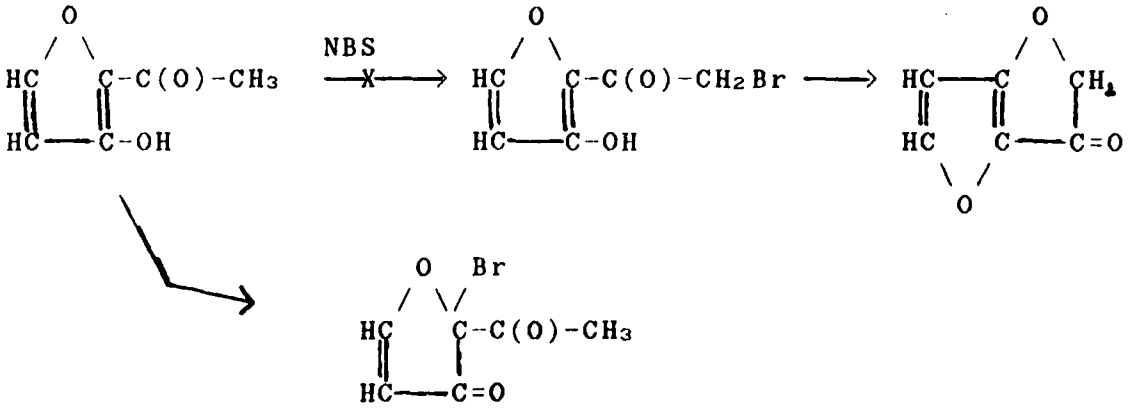
Examples of the [3,2b] ring system exist where Z = Z' = "N"[34], Z = Z' = "S"[35], or Z = "O" and Z' = "N",[36] but no examples of the furo[3,2b]-furan ring system where Z = Z' = "O" have been previously prepared, although the saturated derivatives, the bicyclo[3.3.0]-2,6-dioxaoctanes are known[1].

Several synthetic routes into the furo[3,2b]furan ring system were investigated, based on derivatives of 3-hydroxyfurans. For example, condensation of 3-methoxyfuran with nitroethylene, in anology to a similar reaction observed in unsubstituted furan[37], should give 3-methoxy-2-(2-nitroethyl)furan which would be expected to yield the desired ring system upon hydrolysis. Tetronic acid[38] was converted to its methyl ester[39,40]

by reaction with trimethylorthoacetate in 82%. Attempted reduction by various reducing agents, including DIBAL,[41] failed to give the desired 3-methoxyfuran needed for condensation with nitroethylene.



A more facile entry into 3-oxygenated furans was available through the controlled hydrolysis of alpha-(+)-lactose to give 2-acetyl-3-hydroxy-furan (isomaltol) in 8% yield.[42] Functionalization of the methyl alpha to the ketone followed by cyclization should give the desired furo[3,2b]-furan. Unfortunately, no functionalization could be effected. Bromination[43] with N-bromosuccinimide took place exclusively at C-2 of the furan ring.



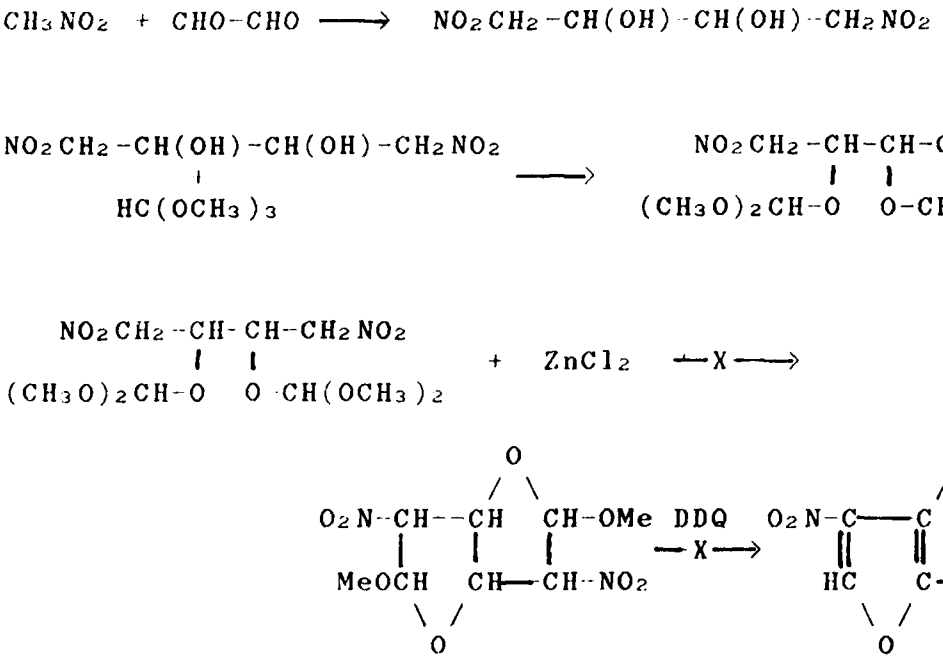
Blocking the C-3 hydroxyl group of 3-hydroxy-2-acetylfuran by acetate gave 3-acetoxy-2-acetylfuran which resisted all attempts at bromination or acid-catalyzed functionalization. More exotic techniques involving formation of silyl enol ether of the ketone[44] or double deprotonations with hexamethyldisilazide followed by bromination also failed to give ring closed products. Similarily, chlorination with phosphorus trichloride,[45] oxalyl chloride or thionyl chloride failed to give ring closed products. Nitration of 3-acetoxy-2-acetylfuran under a number of conditions failed to give characterizable nitro derivatives.

Consequently, a new synthetic strategy to furo[3,2b]furan was developed in which the required furofuran bicyclic ring system would be prepared with the simultaneous introduction of two of the desired nitro groups. Nitromethane is known to react with trimethylorthoformate in the presence of a Lewis acid catalyst such as zinc chloride to give the corresponding formyl derivative as the dimethyl acetal.[46]

$$CH_3-NO_2 + CH(OCH_3)_3 \longrightarrow O_2N-CH_2-CH(OCH_3)_2$$

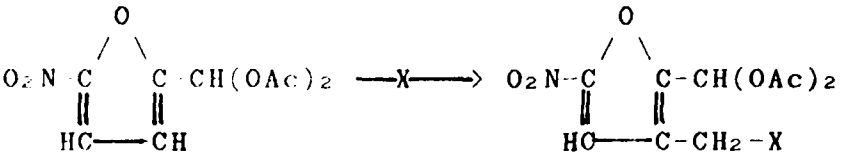
The diacetal potentially available from the reaction between D,L-1,4-dinitro-2,3-butanediol[47,48] and trimethylorthoformate might be internally coupled by a similar zinc chloride catalysis to give a key intermediate in the synthesis of 3,6-dinitrofuro[3,2b]furan. Condensation of nitromethane with 40% aqueous glyoxal gave meso- and D,L-1,4-dinitro-2,3-butanediols in 20% and 18% yield. Reaction of these diols with trimethyl orthoformate gaves the corresponding bis orthoformates. Unfortunately, reaction of the orthoformates with a variety of catalysts such as zinc chloride, zinc bromide, iron chloride, titanium tetrachloride or alkyl aluminium halides failed to give 3,7-dimethoxy-4,8-dinitro-2,6-dioxabicyclo[3.3.0]octane. Refluxing the crude reaction mixtures with DDQ led not to 3,6-dinitro-

furo[3,2b]furan, but to 1,4-dinitrobutadiene.



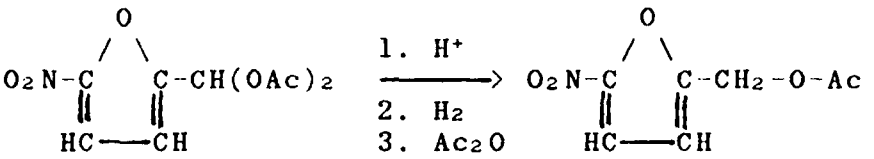
Attempted Preparation of Furo[3,4b]furan

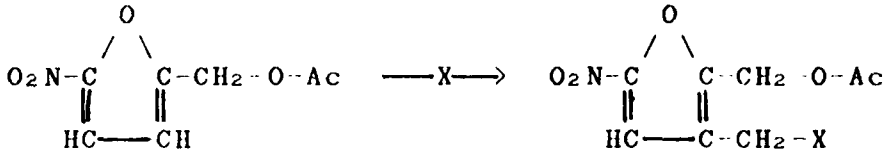
Key intermediates in the attempted synthesis of polynitrofuro[3,4b]-furans were expected to be the readily available 5-nitro-2-furaldehyde and ethyl 5-nitrofuranate. Attempts to chloromethylate or bromomethylate 5-nitrofuranaldehyde diacetate by several known[49] methylation methods were unsuccessful, and unreacted starting material was recovered; the presence of the C-5 nitro group evidently deactivates the furan nucleus towards electrophilic substitution.



It appeared that acetate hydrolysis may be occuring initially and, as a consequence, the furan nucleus is further deactivated toward electro-

philic substitution. Consequently, 5-nitro-2-furanmethanol[50] was prepared in 40% yield and then acetylated by standard methods to give 5-nitro-2-furanmethanol acetate[50] in 73% yield.

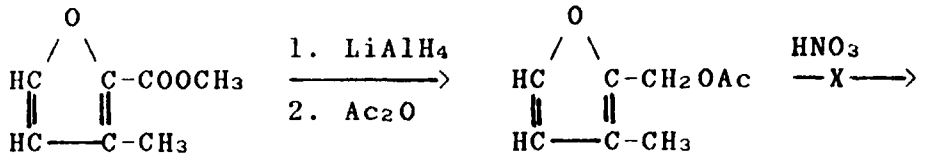




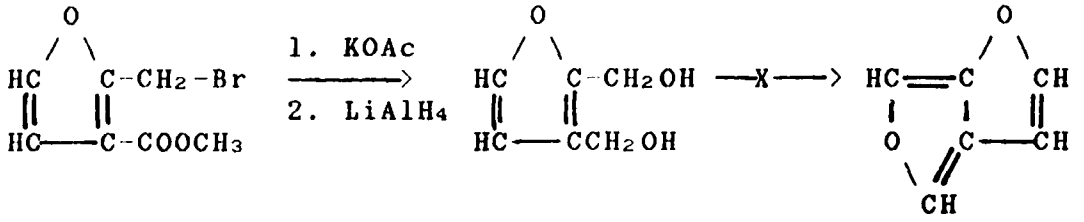
However, 5-nitro-2-furanyl acetate was resistant to both chloromethylation and bromomethylation, and unaltered starting material was recovered. Use of $FeCl_3$, $ZnCl_2$ or $AlCl_3$ as Lewis acid catalysts did not promote the desired halomethylation reaction. A Villsmeir[51] reaction using nitrofuranyl acetate in conjunction with $POCl_3$-DMF at 80°C also gave only unreacted starting material.

In an alternative approach, 2-methyl-3-furanmethanol[49] was prepared from the corresponding ester by lithium aluminium hydride reduction. Allylic bromination of 2-methyl-3-furanmethanol directly with NBS gave none of the desired bromomethylated derivative. The alcohol was subsequently converted to 2-methyl-3-furanmethanol acetate[52] in 94% yield and nitrated in 22% yield to give 5-nitro-2-methyl-3-furanmethanol acetate. Attempted reaction of this nitro acetate with NBS at 80°C (CCl_4) and 110°C (1,2,2-trichloroethane) gave no trace of allylic bromination product with or without added AIBN, benzoyl peroxide or HBr. Direct reaction of the unnitrated acetate with NBS gave the expected 5-bromo-2-methyl-3-furanmethanol acetate[53] rather than 2-bromomethyl derivative.

An attempt was then made to reverse the substitution pattern of nitrofuranmethanol acetate such that the C-2 methyl would no longer be affected by the C-5 nitro group. The readily available ester, methyl 3-methyl-2-furancarboxylate[54] was reduced with lithium aluminum hydride to give 3-methyl-2-furanmethanol[55] in 97% yield. Acetylation gave a 94% yield of 3-methyl-2-furanmethanol acetate. However, even under mild nitration conditions, using acetyl nitrate at -30°C to -15°C, complete destruction of the furan nucleus was encountered.



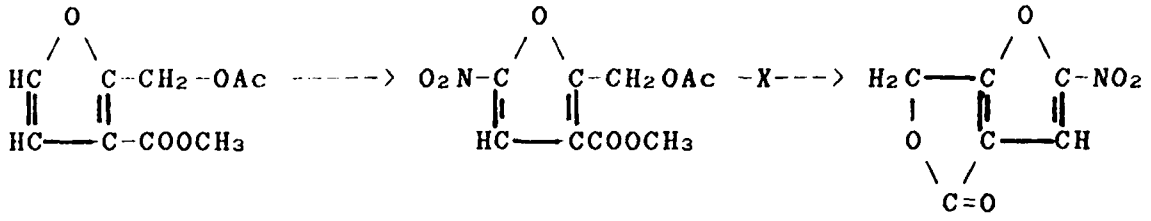
Finally, methyl 2-bromomethyl-3-furanoate was reacted with potassium acetate to give methyl 2-acetoxymethyl-3-furanoate[56] in 78% yield. Subsequent lithium aluminum hydride reduction of the diester gave 2,3-furandimethanol in 44% yield.



Treatment of 2,3-furandimethanol with one equivalent of methanesulfonyl chloride at -30°C provided monomesylate as the predominant product, but furo[3,2b]furan could not be isolated. Rather, spontaneous and rapid decomposition occurred at room temperature in methylene chloride solution within several minutes after low temperature (0°C) workup. Other methods

of ring closure such as methyltriphenoxyphonium trifluoromethane-sulphonate[57] also failed to give the desired product.

Nitration of methyl 2-acetoxymethyl-3-furanoate[56] gave methyl 5-nitro-2-acetoxy-3-furanoate in 27% yield. However, upon treatment with dilute methanolic potassium carbonate, an immediate discoloration of the reaction mixture occurred. Destruction of the furan ring was noted by ^1H NMR spectroscopy after several hours and no ring closed products were observed.



B. EXPERIMENTAL

4-Methoxy-5H-furan-2-one. To a solution of 1.50 g (15.0 mmole) tetronic acid[38] in 25 mL absolute methanol containing approximately 5% (wt) HCl was added 2.4 g (20 mmol) trimethyl orthoacetate and the mixture was refluxed 16 h. The solution was cooled, the solvent evaporated and the residue distilled to give 1.40 g (82%) of 4-methoxy-5H-furan-2-one, bp 94-96°C (0.1 mm) [lit.[39] bp 105°C (0.5 mm)], which crystallized on standing: mp 63°C (lit.[39] mp 63°C);

3-Hydroxy-2-acetylfuran. A solution of 900 mL of absolute ethanol, 255 g (3.0 mol) piperidine, 300 mL (3.0 mol) triethylamine and 180 g (3.0 mol) glacial acetic acid was prepared in a 5 L round bottom flask with mechanical stirring. To the resulting solution at 65°C, was added 1080 g (3.0 mol) of alpha-(+)-lactose monohydrate and the mixture was stirred and heated at 75°C for 24 h. After 900 mL of absolute ethanol was added, the mixture was allowed to stand at ambient temperature for 48 h. The solids which formed were filtered, washed with 200 mL of ethanol and then dissolved in 2 L of hot water. The resulting solution was heated to 90°C, treated with 1 L of 4 M aqueous H_3PO_4, and steam distilled until the distillate gave a negative ferric chloride test for presence of phenol (approximately 2.5 L). The distillate was extracted with 4 X 500 mL of CH_2Cl_2, and the combined organic layers were dried over magnesium sulfate. The solvent was evaporated to give 42 g of yellow solid, which was triturated once with petroleum ether and sublimed at 70-80°C (5 mm) to give 30.1 g (8%) of 3-hydroxy-2-acetylfuran: mp 100-102°C (lit.[42] 101-102°C).

5-Nitro-2-furanmethanol. A mixture of 0.80 g (21 mmol) of lithium aluminium hydride in 70 mL anhydrous ether at 0°C was treated portionwise

with 5.00 g (35.4 mmole) of solid 5-nitro-1-furanaldehyde with brisk stirring. After the addition was complete, the mixture was stirred at 0°C for 5 min, refluxed for 15 min, and then recooled to 5°C. The mixture was treated dropwise sequentially with 0.8 mL of water, 0.8 mL of 15% by weight aqueous sodium hydroxide and 2.5 mL water, and the suspended salts were then removed by filtration. The solvent was evaporated and the residual oil distilled to give 2.0 g (40%) of 5-nitro-2-furanmethanol[50], bp 115-118°C (0.1 mm) [lit.[20] 140-141°C (4 mm)].

5-Nitro-2-furanmethanol Acetate. A solution of 2.0 g (14 mmol) of 5-nitro-2-furfurol in 50 mL anhydrous ether was cooled to 5°C, and 5 mL (70 mmol) pyridine was added, followed by dropwise addition of 3 mL (30 mmol) of acetyl chloride. After 1 h, the resulting mixture was washed with 10 mL of 10% aqueous hydrochloric acid, 10 mL of a saturated sodium bicarbonate solution, dried over magnesium sulfate and the solvent was evaporated. The residual oil was distilled at 104°C (0.1 mm) to give 1.93 g (73%) of 5-nitro-2-furanmethanol acetate, which solidified on standing: mp 39-40°C (lit.[50] mp 41-42°C); ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 3 H), 5.00 (s, 2 H), 6.55 (d, J = 4 Hz, 1 H), 7.15 (d, J = 4 Hz, 1 H).

5-Nitro-2-methyl-3-furanmethanol Acetate. A solution of 5.0 g (49 mmol) of acetic anhydride in 50 mL methylene chloride was cooled to 0°C, and treated dropwise with a solution of 3.0 g (70 mmol) 100% HNO_3 in 10 mL methylene chloride. After 5 min, a solution of 3.80 g (24.6 mmol) 2-methyl-3-furanmethanol acetate[52] in 20 mL methylene chloride was added dropwise at a rate such that the reaction temperature was maintained below 5°C. After 30 min, the mixture was poured into ice-water and the separated aqueous phase extracted with 50 mL of methylene chloride. The combined organic layers were washed with 50 mL of cold aqueous 1 M sodium carbonate solution, dried over magnesium sulfate and the solvent

evaporated. The residual red oil was chromatographed on slica gel (3:1 hexanes - ether) and distilled at 130-131°C (0.4 mm) to give 1.10 g (22%) of 5-nitro-2-methyl-3-furanmethanol acetate: NMR ($CDCl_3$) δ 7.22 (s, 1 H), 4.83 (s, 2 H), 2.45 (s, 3 H), 2.05 (s, 3 H).

Anal. Calcd for $C_8H_9NO_5$: C, 48.25; H, 4.55; N, 7.03. Found: C, 48.16; H, 4.70; N, 6.88.

3-Methyl-2-furanmethanol Acetate. A solution of 3.1 g (28 mmol) of 3-methyl-2-furanmethanol and 7.0 mL dry pyridine in 100 mL methylene chloride was cooled to 0°C and a solution of 4.5 g (57 mmol) acetyl chloride in 10 mL methylene chloride was added dropwise. The mixture was stirred and allowed to come to room temperature over 16 h, washed with 100 mL of 10% aqueous hydrochloric acid and the aqueous phase extracted with 50 mL of methylene chloride. The combined organic layers were washed with 100 mL of aqueous 1 M sodium bicarbonate solution, dried over magnesium sulfate and the solvent was evaporated. The residual oil was distilled at 72-73°C (5 mm) to give 4.00 g (94%) of 3-methyl-2-furanmethanol acetate: bp 72 - 73°C(5 mm); NMR ($CDCl_3$) δ 2.03 (s, 6 H), 4.90 (s, 2 H), 6.07 (d, J = 2 Hz, 1 H), 7.18 (d, J = 2 Hz, 1 H).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.64; H, 6.71.

2,3-Furandimethanol. A rapidly stirring mixture of 4.00 g (0.105 mmol) of lithium aluminium hydride in 200 mL anhydrous ether at 5°C was treated dropwise with a solution of 10.00 g (50.5 mmole) methyl 2-acetoxymethyl-3-furanoate[56] in 25 mL ether. After the addition was completed, the mixture was refluxed for 30 minutes, cooled to 20°C, and 4 mL water, 4 mL of aqueous 15% sodium hydroxide solution and 12 mL water were added successively dropwise. After it was stirred at ambient

temperature for 60 min, the suspension was filtered and the filter cake was washed with 50 mL of ether and 50 mL of tetrahydrofuran. The filtrate was stripped of solvent and the residual oil (3.6 g) was chromatographed on silica gel (3:1 ethyl acetate-hexanes) to give 2.85 g (44%) of 2,3-furandimethanol as a viscous oil: NMR ($CDCl_3$) δ 4.25 (br s, 3 H), 4.30 (br s, 3 H), 6.18 (d, J = 2 Hz, 1 H), 7.15 (d, J = 2 Hz, 1 H).

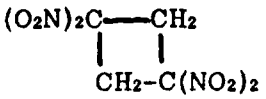
Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29.. Found: C, 55.88; H, 6.41.

Methyl 5-Nitro-2-acetoxymethyl-3-furancarboxylate. To a solution of 20 g (0.20 mole) acetic anhydride in 50 mL of methylene chloride was added, dropwise, 8.0 g (0.127 mole) of 100% nitric acid in 50 mL of methylene chloride at 0°C, and then 3.00 g (15.1 mmole) of methyl 2-acetoxymethyl-3-furancarboxylate in 10 mL methylene chloride. The resultant mixture was allowed to reach room temperature slowly and stirring was continued for 6 h. The solution was extracted with 2 X 100 mL of aqueous 1 M sodium bicarbonate, dried over magnesium sulfate and the solvent was evaporated. The residual oil was chromatographed on silica gel (2:1 hexane-ether) to give 1.00 g (27%) of methyl 5-nitro-2-acetoxymethyl-3-furancarboxylate, as an oil: ^1H NMR ($CDCl_3$)δ2.05 (s, 3 H, $COCH_3$), 3.82 (s, 3 H, CO_2CH_3), 5.30 (s, 2 H, $-CH_2O-$), 7.40 (s, 1 H, C=C-H); IR (film) 1740 (C=O) cm^{-1}, 1520 (NO_2) cm^{-1}.

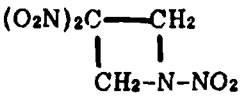
IV. POLYNITRO CYCLOBUTANES.

A. DISCUSSION

As an extension of previous work on polynitro derivatives of oxetanes and azetidines, work was begun on the synthesis of 1,1,3,3-tetranitrocyclobutane (TNCB). Selection of this target molecule was prompted by the experimentally based observation of the heat of formation of 1,3,3-trinitroazetidine (TNA) by R. Willer.[58] Calculation of the monopropellant Isp of TNA based on this heat of formation gave a value of 273.4 compared to 267.4 for HMX. Cyclobutane rings have comparable strain energy to azetidine rings. Comparision of densities calculated by the Willer and Chaffin program for TNA and TNCB are summarized.



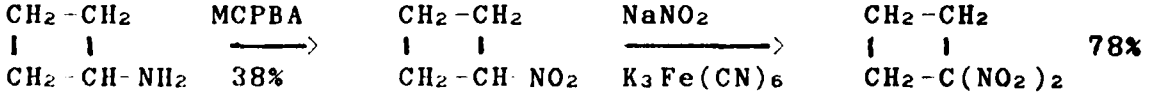
(TNCB)



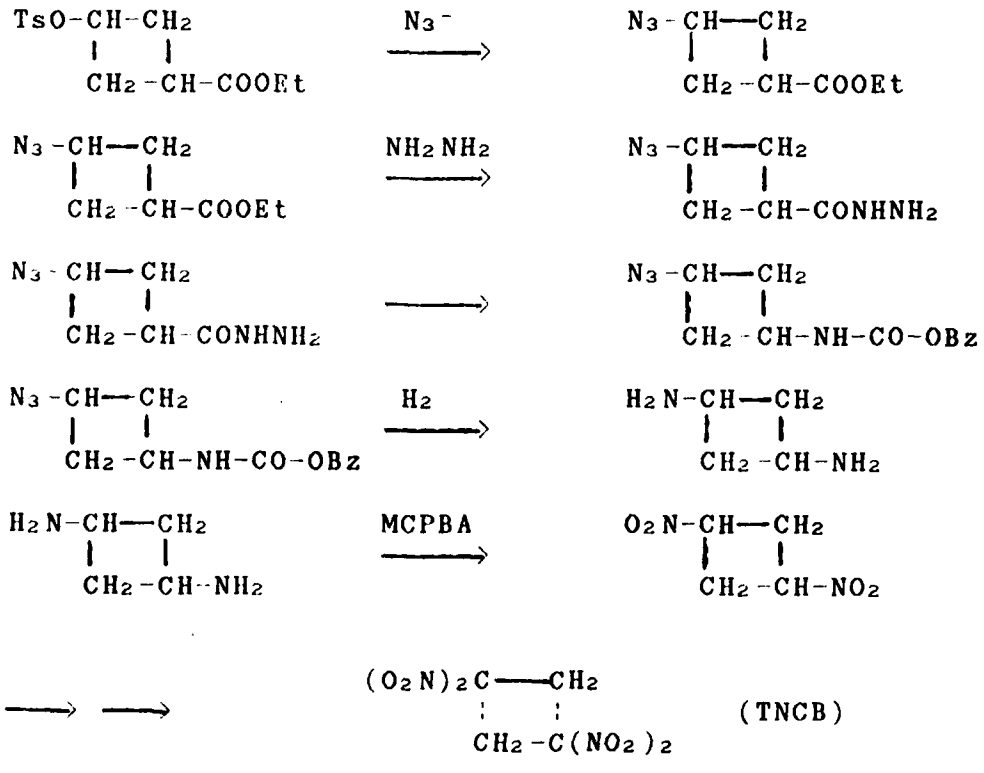
(TNA)

	(TNCB)	(TNA)	(HMX)
Density	1.82	1.82	1.88
Isp		273.4	267.4

Prior to this work, the only nitro derivatives of cyclobutane known were 1-nitrocyclobutane[59] and 1-bromo-1-nitrocyclobutane,[60] although the recently prepared 1,4-dinitrocubane[61] also contains a nitro group on a four member ring in a polycyclic system. A model system for the preparation of TNCB, the previously unknown 1,1-dinitrocyclobutane was prepared from 1-aminocyclobutane[62] by m-chloroperbenzoic acid oxidation (38% yield) followed by oxidative nitration with sodium nitrite in the presence of potassium ferricyanide (78% yield). This geminal dinitrocyclobutane was isolated as a liquid with a density of 1.26 (Calc. 1.28).



The isomer of this compound, 1,3-dinitrocyclobutane was then prepared by a multi-step synthetic route based on the oxidation of 1,3-diaminocyclobutane. Ethyl 3-azidocyclobutanecarboxylate was synthesized in 92% yield from sodium azide displacement of ethyl 3-p-toluenesulfonatocyclobutanecarboxylate[63] and in 50% from ethyl 3-chlorocyclobutanecarboxylate.[65] This azido ester was converted to 3-azidocyclobutanecarboxylic acid hydrazide with 85% hydrazine hydrate in 60% yield. The hydrazide was converted to benzyl N-(3-azidocyclobutyl) carbamate with sodium nitrite in benzyl alcohol, in 71% yield. This carbamate was subsequently reduced and hydrolyzed to 1,3-diaminocyclobutane[65] in 50% yield. Oxidation of 1,3-diamino cyclobutane with m-chloroperbenzoic acid in refluxing dichloroethane gave 1,3-dinitrocyclobutane in 38% yield.



Conversion of 1,3-dinitrocyclobutane to 1,1,3,3-tetranitrocyclobutane is under study.

B. EXPERIMENTAL.

1,1-dinitrocyclobutane. A solution of 0.60 g (5.9 mmol) of nitrocyclobutane[59] and 0.39 g (9.6 mmol) of sodium hydroxide in 5 mL of water was stirred at 23°C for 45 min, cooled to 0°C and 5 mL of methylene chloride was added. This mixture was treated successively with a solution of 1.67 g (24 mmol) of sodium nitrite in 3 mL of water, a solution of 0.40 g (1.19 mmol) of potassium ferrocyanide in 3 mL of water, and finally 1.41 g (5.9 mmol) of solid sodium persulfate. The mixture was stirred 15 min at 0°C and 1 h at 23°C. The layers were separated and the aqueous layer was extracted with 2 x 15 mL of methylene chloride. The combined organic layers were washed with 3 x 20 mL of saturated sodium chloride solution, dried over magnesium sulfate and evaporated to give 0.68 g (78%) of 1,1-dinitrocyclobutane as an oil. An analytical sample was prepared by column chromatography on silica gel (1:10 ethyl acetate - hexane) followed by molecular distillation at 100°C (0.5 mm): IR (film) 3030 (m), 2945 (mw), 1562 (s), 1420 (ms) cm^{-1}; NMR ($CDCl_3$) δ 2.2 (m, J = 8.5 Hz, 2 H), 3.18 (t, J = 8.5 Hz, 4 H) ppm.

Anal. Calcd for $C_4H_6N_2O_4$: C, 32.88; H 4.14; N, 19.18. Found: C, 33.12; H, 4.20; N, 19.40.

Ethyl 3-Azidocyclobutanecarboxylate. A mixture of 2.61 g (32 mmol) of sodium azide and 6.2 g (21 mmol) of ethyl 3-p-toluenesulfonatocyclobutanecarboxylate[63] in 10 mL of ethanol and 5 mL of water was refluxed for 23 h. The mixture was cooled, diluted with 20 mL of water and extracted with 4 x 50 mL of ether. The combined ether solutions were washed with 2 x 40 mL of water and 2 x 40 mL of saturated sodium chloride solution, dried over magnesium sulfate and solvent was evaporated. The residual oil was distilled at 74-75°C (4.0 mm) [lit.[65] 94°C (5 mm)] to give 3.27 g (92%) of ethyl 3-azidocyclobutanecarboxylate: IR (CH_2Cl_2) 2150 ($-N_3$)

cm^{-1}; NMR ($CDCl_3$)δ1.2 (t, J = 7.5 Hz), 3 H), 2.4 (m, 4 H), 3.6 (m, 2 H), 3.9 (q, J = 7.5 Hz, 2 H).

3-Azidocyclobutanoyl Hydrazide. A mixture of 13.22 g (78 mmol) of ethyl 3-azidocyclobutanecarboxylate and 7.67 g (159 mmol) of hydrazine hydrate was heated at 95-104°C for 30 min. The excess hydrazine was evaporated and the residue recrystalized from ether-hexane to give 6.86 g (57%) of 3-azidocyclobutanoyl hydrazide, mp 72-75°C (lit.[65] 76°C).

Benzyl N-(3-Azidocyclobutyl)-carbamate. To a mixture of 5.0 g (32 mmol) of 3-azido-cyclobutanoyl hydrazide, 68 mL of 1 M aqueous hydrochloric acid and 40 mL of ether at °C, was added dropwise over 15 min a solution of 3.0 g (43.5 mmol) of sodium nitrite in 15 mL of water. The layers were separated and the aqueous phase was extracted with 2 x 40 mL of ether and the combined organic layers were dried over calcium chloride. The dried ether solution was mixed with 13.5 g (125 mmol) of benzyl alcohol and the solvent evaporated over 2 h. The residue was recrystallized from ether-hexane to give 5.58 g (71%) of benzyl N-(3-azidocyclobutyl)-carbamate, mp 61-64°C (lit.[65] 66°C): IR (CH_2Cl_2) 2150 cm^{-1}; NMR ($CDCl_3$)δ1.9-3.0 (m, 5 H), 3.4-4.3 (m, 2 H), 5.05 (s, 2 H), 7.25 (s, 5 H).

1,3-Diaminocyclobutane. A mixture of 5.58 g (22.7 mmol) of benzyl N-(3-azido-cyclobutyl)-carbamate and 1.0 g of 20% palladium hydroxide on carbon in 200 ml 95% ethanol was hydrogenated at 45 psi in a Parr apparatus until IR analysis of an alliquot showed the absence of organic azide absorbance at 2100 cm^{-1}. The gas phase was evacuated and replaced with fresh hydrogen every 21 h until the reaction was complete. The catalyst was removed by filtration, the solvent evaporated, and the residue was distilled at 80° (1.0 mm) (lit.[65] 90°C (0.55)) to give 0.43 g (22%) of 1,3-

diaminocyclobutane: IR (film): 3100-3650 (s), 3000 (s), 1620 (ms), 1470 (ms), 1380 (ms), 1250 (m), 1085 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.6 (bs, 4 H); 2.0-3.0 (m, 4 H); 3.5 (m, 2 H).

1,3-Dinitrocyclobutane. A solution of 0.70 g (8.13 mmol) of 1,3-diaminocyclobutane in 6 mL of 1,2-dichloroethane was added dropwise to a refluxing solution of 9.8 g (56.9 mmol) of m-chloroperbenzoic acid in 100 mL of 1,2-dichloroethane. The mixture was refluxed for 3 h, cooled to ambient temperature and filtered, and the solids were washed with 3 x 30 mL of 1,2-dichloroethane. The combined organic fractions were washed with 2 x 25 mL of 5% aqueous sodium carbonate solution and with 2 x 25 mL of saturated sodium chloride solution and dried over magnesium sulfate. The solvent was evaporated and the residue was purified by bulb to bulb distillation at 100°C (1.5 mm) to give 0.45 g (38%) of 1,3-dinitrocyclobutane: IR (CH_2Cl_2) 1550, 1400, 1380 cm^{-1}; NMR ($CDCl_3$)δ 2.6-3.6 (m, 4 H), 4.74 (m, 1 H), 5.05 (m, 1 H).

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